

LA-UR- 03-2385

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Submitted to: Sixth International Conference On
Methods and Applications of Radioanalytical Chemistry
Kailua-Kona, Hawaii, April 7 - 11, 2003



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Form 836 (8/00)

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RAPID SEPARATION OF FRESH FISSION PRODUCTS

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ABSTRACT

The fission of highly enriched uranium by thermal neutrons creates dozens of isotopic products. The Isotope and Nuclear Chemistry Group participates in programs that involve analysis of “fresh” fission products by beta counting following radiochemical separations. This is a laborious and time-consuming process that can take several days to generate results. Gamma spectroscopy can provide a more immediate path to isotopic activities, however short-lived, high-yield isotopes can swamp a gamma spectrum, making difficult the identification and quantification of isotopes on the wings and valley of the fission yield curve.

The gamma spectrum of a sample of newly produced fission products is dominated by the many emissions of a very few high-yield isotopes. Specifically, ¹³²Te (3.2 d), its daughter, ¹³²I (2.28 h), ¹⁴⁰Ba (12.75 d), and its daughter ¹⁴⁰La (1.68 d) emit at least 18 gamma rays above 100 keV that are greater than 5% abundance. Additionally, the 1596 keV emission from ¹⁴⁰La imposes a Compton background that hinders the detection of isotopes that are neither subject to matrix dependent fractionation nor gaseous or volatile precursors. Some of these isotopes of interest are ¹¹¹Ag, ¹¹⁵Cd, and the rare earths, ¹⁵³Sm, ¹⁵⁴Eu, ¹⁵⁶Eu, and ¹⁶⁰Tb.

C-INC has performed an HEU irradiation and also “cold” carrier analyses by ICP-AES to determine methods for rapid and reliable separations that may be used to detect and quantify low-yield fission products by gamma spectroscopy. Results and progress will be presented.

INTRODUCTION

C-INC conducts radiochemical exercises to measure chemist proficiency and maintain the capability to perform radiochemical separations. These exercises consist of irradiation of a highly enriched uranium target by thermal neutron bombardment, target dissolution, gamma spectroscopy, and separations of individual radioelements and quantification by beta counting. From the several initial gamma counts, we are able to determine precise activities, and therefore neutron flux information, from several isotopes, specifically ¹⁴⁰Ba, ⁹⁹Mo, and ⁹⁵Zr. However, we are interested in prompt confirmation using activities of lower yield isotopes.

EXPERIMENTAL

This work was conducted as three parallel sets of experiments due to the need to first complete programmatic tasks upon target receipt. When time permitted, experiments were then performed

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as soon as possible before target activity could appreciably decay. Additionally, the inability to perform further irradiations prior to this report led us to investigate separation of the rare-earths using cold carriers only.

A 112 mg target foil of 93.5% HEU supplied by C-INC was irradiated at the MITR-II reactor at the Massachusetts Institute of Technology to produce approximately $1.9\text{E}14$ fissions. The target was allowed to decay for more than a day before being shipped to LANL for analysis. Upon receipt, the target was dissolved and volumetrically diluted for aliquotting. A 1% aliquot was immediately sent for gamma spectroscopy. It was counted on a 14% efficient, Al-endcap detector at a distance of 15 cm for 10 minutes. The sample was counted 4.3 days from the end of bombardment (EOB). The spectrum is shown below in Figure 1.

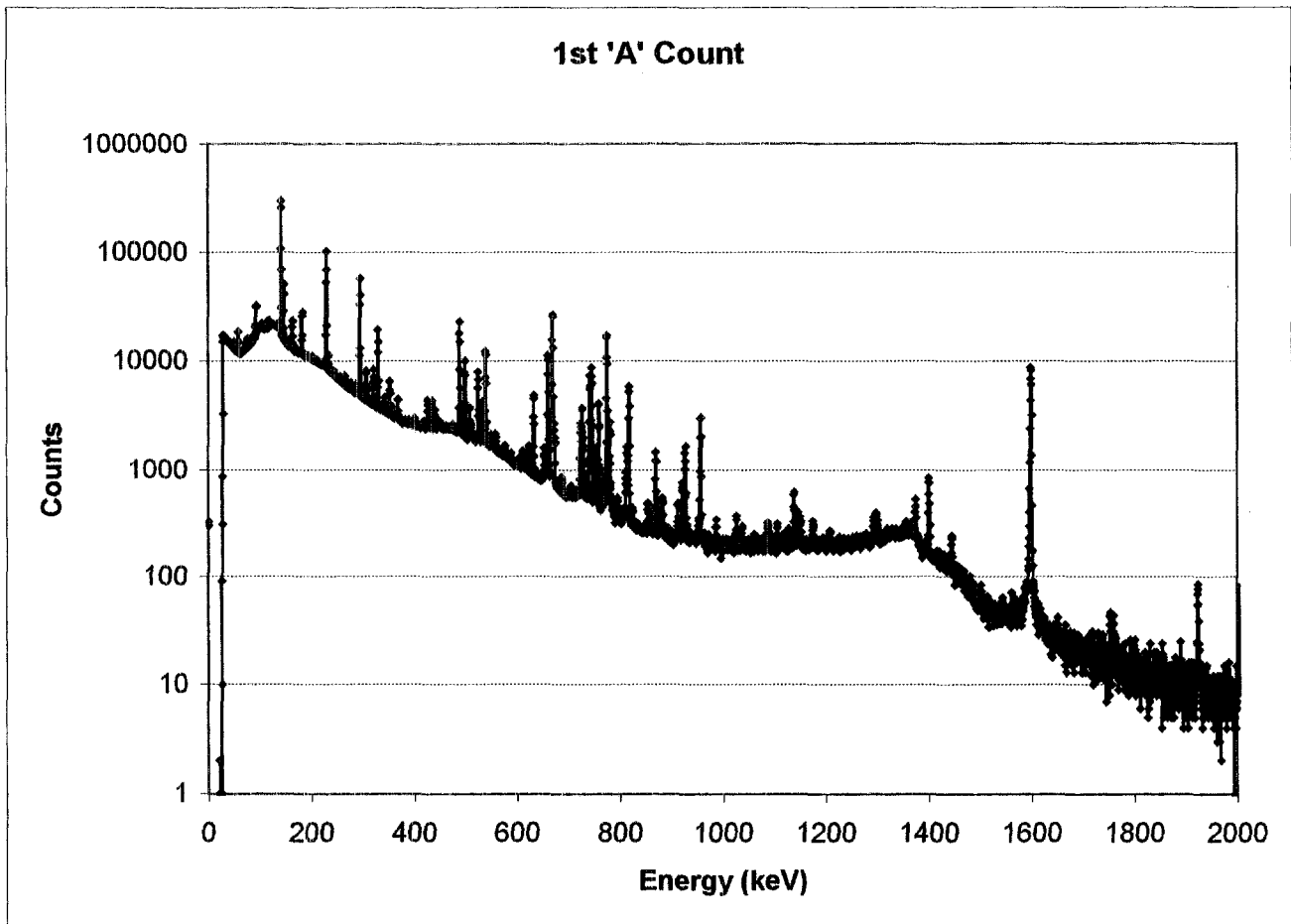


Figure 1

This spectrum was analyzed using RAYGUN, a precursor to the development of GAMANAL. It is a rather simple spectral analysis tool that has been in use at LANL for decades. RAYGUN initially searches a spectrum and determines background regions. It then searches non-background regions and determines peaks, resolves multiplets, and provides peak area information. It then performs isotope identification by user-defined libraries. A listing of the identified peaks for this spectrum is in Table 1.

Isotopes Identified in Initial Count					
keV	Isotope	keV	Isotope	keV	Isotope
91.0	Nd-147	364.5	I-131	739.6	Mo-99
116.4	Te-132	423.8	Ba-140	751.8	La-140
131.1	La-140	432.6	La-140	756.9	Zr-95
133.4	Ce-144	437.7	Ba-140	766.0	Nb-95
140.5	Mo-99	487.1	La-140	772.8	I-132
145.4	Ce-141	497.2	Ru-103	778.1	Mo-99
162.6	Ba-140	522.7	I-132	812.5	I-132
181.1	Mo-99	531.1	Nd-147	816.0	La-140
228.3	Te-132	537.4	Ba-140	868.0	La-140
242.0	La-140	610.6	Ru-103	919.7	La-140
266.6	La-140	630.3	I-132	925.4	La-140
293.3	Ce-143	667.8	I-132	951.3	La-140
304.9	Ba-140	671.1	I-132	954.8	I-132
319.4	Nd-147	724.3	Zr-95	1136.4	I-132
328.8	La-140	727.3	I-132	1596.5	La-140

Table 1

Figure 1 illustrates how the 1596 keV gamma ray from ^{140}La is not only the most prominent peak in the spectrum, but also how it is the largest contributor to the Compton background. Table 1 highlights how an early count is dominated by peaks from the Ba/La and Te/I parent-daughter pairs. Removal of these isotopes would certainly facilitate detection and quantification of other less active species.

One experiment was to first remove Ba from the sample to preclude further ingrowth of ^{140}La . It would be expected that La would be carried with the other trivalent rare earth isotopes of interest. A subsequent separation of the lanthanides would then be necessary.

An aliquot of approximately 0.5% of the dissolved target was taken one week after the original dissolution (approximately 10 days after EOB) and the following process performed:

- Initial gamma count obtained,
- 20 mg of Ba carrier added,
- 1 ml of concentrated HCl added to precipitate BaCl_2 ; the precipitate counted for yield,
- 2 mg each of La and Fe added to supernate and precipitated with concentrated NH_4OH ,
- supernate and precipitate each gamma counted for yield.

These simple steps were accomplished and counting data completed in less than 90 minutes. The procedure was completed several times and Table II summarizes typical results. The detectable rare earth isotopes were effectively removed from Ba, and it would be expected that Sm, Eu and Tb isotopes would behave similarly.

	Original Count	BaCl ₂ Ppt		Fe/La Ppt		Supernate	
	Atoms	Atoms	Yield	Atoms	Yield	Atoms	Yield
⁹⁵ Zr	6.89E+10	1.91E+08	0.003	6.57E+10	0.953		
¹³⁷ Cs						5.41E+10	??
¹⁴⁰ Ba	6.53E+10	6.03E+10	0.924			3.82E+09	0.059
¹⁴⁰ La	3.54E+11	1.36E+10	0.038	6.69E+10	1.013		
¹⁴¹ Ce	6.01E+10			5.93E+10	0.987		
¹⁴³ Ce	6.55E+10			6.04E+10	0.922		
¹⁴⁴ Ce	7.20E+10			7.77E+10	1.080		
¹⁴⁷ Nd	2.24E+10			2.15E+10	0.958		

Table II

A second independent experiment was to remove ¹³²Te, and thus the source for ¹³²I. The following steps were performed:

- Initial gamma count of approximately 0.5% of the dissolved target,
- Addition of 5.3 mg of stable Te carrier,
- Reduction of the sample over flame and redissolution in concentrated HCl several times to convert to chloride form,
- Dissolution of the residue in 1 ml of 6M HCl,
- Addition of the solution to a 2 ml column of AG 1x8 resin preconditioned with 6M HCl,
- Addition of four 1 ml washes of 6M HCl.
- All eluants were caught and gamma counted as one sample, and
- The resin was slurried from the column with water and also gamma counted.

Table III contains counting results and calculated yields for the above procedure. In this case, ¹³²Te and ¹³²I were strongly retained on the resin and well separated from the rare earths. The apparent loss of ¹³²Te is likely due to the geometry effect of counting the solid resin which had settled in the liquid.

Isotope	Initial dpm	Eluant dpm	Resin dpm	Eluant Yield	Resin Yield
¹³² Te	3.076E+05		2.430E+05		0.790
¹⁴⁰ Ba	2.931E+05	2.633E+05		0.898	
¹⁴¹ Ce	1.306E+05	1.194E+05	3.254E+02	0.914	0.002
¹⁴³ Ce	4.225E+05	4.557E+05		1.078	
¹⁴⁷ Nd	1.267E+05	1.109E+05		0.876	

Table III

The third experiment involved separation of Ag, Cd, and the individual rare earths from Ba. Due to an administrative hold on handling of alpha-emitting materials, additional HEU targets could not be prepared for irradiation prior to this report. Therefore, mixtures of stable carriers were prepared for investigation of separation schemes to be analyzed by inductively coupled plasma –

atomic emission spectroscopy (ICP-AES). This alternative technique is applicable to this project as it is intended to be employed for yielding of rapid radiochemical procedures.

As stated previously, removal of Ba is of primary interest to preclude further ingrowth of ^{140}La . It is expected that in the method below, Ag and Cd would follow Ba in the separation, isolating these elements from the rare earths. The insoluble AgCl could then be yielded gravimetrically. The Ba is separated as carbonate from the Cd, which is then analyzed by ICP-AES. The rare earth supernate is then converted to a dilute HNO_3 solution.

From the work by Pin¹, et al., a rare earth separation scheme using Eichrom² Ln resin was developed. This enables removal of La from a fraction containing Sm, Eu and Tb. The separation scheme is described as follows:

- The following masses of stable carriers are added to a 250-mL Erlenmeyer flask:
 - Ag 9.98 mg
 - Cd 9.94 mg
 - Ba 10.00 mg
 - La 0.99 mg
 - Ce 0.99 mg
 - Nd 0.98 mg
 - Sm 0.98 mg
 - Eu 0.99 mg
 - Tb 0.99 mg
- Add 20 ml concentrated HNO_3 to the flask and reduce volume to ~5 ml over heat.
- Transfer the solution to a centrifuge cone using 4M HNO_3 .
- Place the cone into an ice bath. While stirring add 30 ml fuming HNO_3 and 16 drops concentrated HCl .
- Let solution sit in an ice bath for 30 minutes – AgCl , CdCl_2 and $\text{Ba}(\text{NO}_3)_2$ will precipitate.
- Centrifuge and decant the supernate into a 250 ml Erlenmeyer and proceed to rare earth separation below.
- Add 10 ml DI water to the precipitate and stir. The CdCl_2 and $\text{Ba}(\text{NO}_3)_2$ will dissolve, leaving the AgCl as a solid.
- Centrifuge and decant the supernate into a clean cone. Wash the precipitate with water, centrifuge and add wash to the cone containing the supernate. Obtain gravimetric yield of the AgCl precipitate.
- Add enough NH_4OH to the supernate to bring the pH to 9. Add 3 ml of saturated $(\text{NH}_4)_2\text{CO}_3$. Place in a hot bath and allow the BaCO_3 to precipitate and measure gravimetrically for yield.
- Centrifuge and decant supernate into a new tube marked as Cd sample. Dilute 1:1000 and analyze by ICP-AES.

Rare earth separation:

¹ C. Pin, J. F. S. Zalduogui, *Analytica Chimica Acta* 339 (1996) 79-89.

² Eichrom Technologies, Inc., 8205 S. Cass Ave. Suite 106, Darien, IL 60561

- Bake down the rare-earth solution in the Erlenmeyer flask. Bring up in several ml 0.05M HNO₃. Repeat this step several times and transfer to a centrifuge cone.
- Bake down one more time and bring up in 1.0 ml of 0.05M HNO₃.
- Add this to a pre-prepared column (0.8 cm x 4 cm) containing 1.6 g of Eichrom Ln resin, conditioned with 1M HCl. Catch the eluant and dilute to 50.0 ml.
- Rinse the centrifuge cone with 1.0 ml of 0.25M HCl and add to the column. Catch the eluant and dilute to 50.0 ml. Repeat this 9 times.
- Add 1.0 ml of 0.75M HCl to the column, catch the eluant and dilute to 50.0 ml. Repeat this 3 times.
- Analyze each eluant by ICP-AES.

The gravimetric yields of Ba and Ag were both >96% indicating effective removal of Ba from the other species. If this had been performed on an actual irradiation, the AgCl precipitate would be analyzed by gamma spectroscopy for quantification of ¹¹¹Ag and carryover of ¹⁴⁰Ba. This is planned as future work.

The ICP-AES analysis of the Cd fraction indicated complete recovery of Cd and no detectable Ba in the sample.

Each rare earth eluant was analyzed by ICP-AES in series to determine the effectiveness of separation of La, Ce and Nd from the heavier elements. The results indicated that the low-yield isotopes of Sm, Eu and Tb can be completely isolated and yielded using this method. Figure II below shows graphically the fractional elution of each of the rare earths relative to each other.

The above separations required less than four hours to complete which would be satisfactory to qualify as a rapid method in this case. However, with optimization of certain steps and practice, separation and analysis could reasonably be reduced to 2-3 hours.

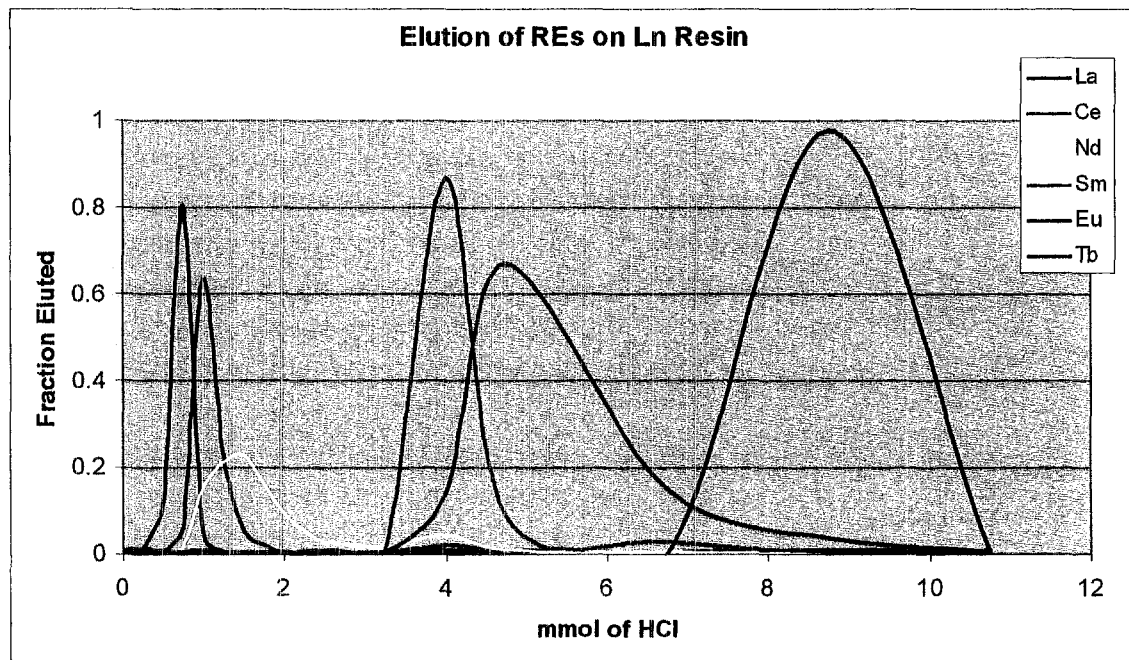


Figure II

CONCLUSIONS

These independent experiments indicate that $^{132}\text{Te}/^{132}\text{I}$ and $^{140}\text{Ba}/^{140}\text{La}$ parent-daughter pairs can be removed from the low-yield isotopes of interest (^{111}Ag , ^{115}Cd , ^{153}Sm , ^{154}Eu , ^{156}Eu , and ^{160}Tb), allowing their detection by gamma spectroscopy soon after irradiation.

FUTURE WORK

When HEU target irradiations are resumed, it is our intention to integrate these separation schemes into a single method which can be performed rapidly and reliably. This will likely include precipitation of $^{111}\text{AgCl}$, followed by gravimetric yielding and gamma spectroscopy. ^{115}Cd will also be separated, yielded by ICP-AES and counted by gamma spectroscopy. The isotopes of Sm, Eu and Tb will subsequently be isolated from ^{140}La , ^{147}Nd , and Ce isotopes, yielded by ICP-AES, and counted by gamma spectroscopy.

Minimization of the time to perform these separations and analyses will contribute to making rapid quantification a useful analytical tool in our radiochemistry program.